Polymerization of 3-Undecylbithiophene and Preparation of Poly(3-undecylbithiophene)/Polystyrene Composites in Supercritical Carbon Dioxide

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ABSTRACT: The polymerization of 3-undecylbithiophene in supercritical carbon dioxide (with ferric triflate as the oxidant) was studied at 313 K and 10.5 MPa. The resulting polymer was comparable in structure, molecular weight, conjugation, and intrinsic electrical conductivity to the polymer synthesized in nitrobenzene (with ferric chloride as the oxidant). In addition, a 95% yield of the conducting polymer was obtained in 1 h. Conductive composites of poly(3-undecylbithiophene) and porous, cross-linked polystyrene were prepared via the in situ polymerization of 3-undecylbithiophene in supercritical carbon dioxide at temperatures in the range 313−413 K and pressures in the range 10.5−34.5 MPa. The highest conductivities of the composite were obtained at 313 K and 20.7 MPa, which represent optimum conditions for oxidant/monomer deposition and conducting polymer network formation on the surface and pores of the host polymer.

Introduction

Electrically conducting polymers such as polythiophenes and polypyrroles are of interest in a number of applications, including dye-sensitized titanium dioxide solar cells,[1] chemical and optical sensors,[2] nonlinear optical devices,[3] light-emitting diodes,[4] and field-effect transistors.[5] Processing of such polymers, however, generally employs a wide variety of organic solvents that are noxious or harmful to the environment. As such, processing with an environmentally benign supercritical fluid such as carbon dioxide offers an attractive alternative to conventional processing with these solvents. The advantages of supercritical carbon dioxide for polymerization and blend formation have been enumerated by several investigators.[6−8] Carbon dioxide is inexpensive and nonflammable, offers high mass transport rates, and allows in situ removal of unreacted monomer and other impurities. Its solvent power can be tuned continuously by changing the pressure and temperature. Supercritical carbon dioxide is also known to swell host polymers,[9] which facilitates processing and blend formation.

The objective of the present work was to study the in situ polymerization of 3-undecylbithiophene in a host substrate using carbon dioxide as the solvent. It has been shown[10] that poly(3-undecylbithiophene) produced by a simple oxidation of 3-undecylbithiophene with ferric chloride in nitrobenzene forms a highly conjugated polymer with properties equal or superior to regioregular poly(3-alkylthiophenes), normally requiring tedious preparation procedures. Since the alkyl side chain is present on every other thiophene unit, there are fewer steric interactions between the side chains than in other conducting polymers such as poly(3-alkylthiophenes).[11] This results in high conductivities and improved environmental stability. However, as in the case of other intrinsically conducting polymers, it is difficult to process poly(3-undecylbithiophene) into useful large articles, and the polymer must therefore be combined with an insulating polymer to yield a composite that is processable and mechanically strong. The insulating polymer can be nonporous (in which case the conducting polymer must diffuse into the nonporous matrix), or it can be porous. In the latter case, the conducting polymer can be deposited as a film inside the porous host, which becomes electrically conducting as a result of the connected network of conducting polymer films in the pores.[6]

In the present work, the polymerization of 3-undecylbithiophene was studied in supercritical carbon dioxide to establish the feasibility of the reaction and to compare the resulting polymer with the polymer synthesized in nitrobenzene. The in situ polymerization of the monomer in porous, cross-linked polystyrene was also studied. As shown by Park and Ruckenstein,[6] porous, cross-linked polystyrene can be synthesized with uniform pores that provide the structure necessary for the formation of conducting polymer networks. The host polymer also provides mechanical strength to the more fragile conducting polymer.

Experimental Section

Materials. The monomer (3-undecylbithiophene) and the host polymer (porous, cross-linked polystyrene) were synthesized according to procedures described in the literature.[6,10,12] Coleman grade carbon dioxide (99.9% purity) was purchased from Air Products and used as received. Ferric triflate was synthesized by a dropwise addition of trifluoromethanesulfonic acid (32 mL) to a stirred suspension of ferric chloride (55 g) in methylene chloride (50 mL) at room temperature, followed by stirring overnight. A gentle flow of dry nitrogen gas was maintained at all times in order to facilitate removal of hydrogen chloride. Solvent was then removed under reduced pressure (in a rotatory evaporator), and the solid residue was dried under vacuum. A precipitate of ferric triflate formed according to the reaction

$$FeCl_3 + 3CF_3SO_3H \rightarrow Fe(CF_3SO_3)_3 + 3HCl$$

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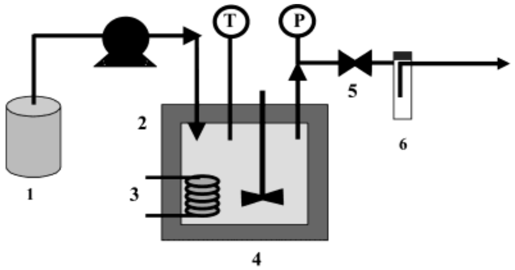
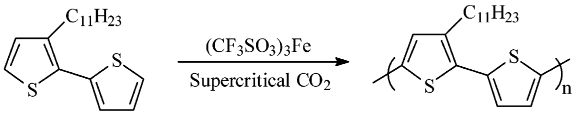


Figure 1. Schematic diagram of the experimental apparatus: 1, CO_2 tank; 2, heating jacket; 3, cooling coil; 4, reactor; 5, depressurization valve; 6, trap.

The ferric triflate was then dried and stored under nitrogen. Porous, cross-linked polystyrene (PS) was prepared according to the procedure described by Park and Ruckenstein.[6] These authors have shown that their procedure yields a polymer with uniform pores of approximately 10 μm. Furthermore, we have shown previously[12] that the porous structure of the polymer prepared in this manner allows supercritical carbon dioxide to diffuse rapidly through the polymer. Also in our previous study,[12] the polymer did not swell appreciably or absorb carbon dioxide at 313 K and 10.5 MPa.

Experimental Apparatus. The experimental apparatus used in the supercritical carbon dioxide studies is shown in Figure 1. It consists of a high-temperature, high-pressure stirred reactor (Paar model 4576) and a high-pressure syringe pump (ISCO model 500D) for pressurizing the carbon dioxide. A cooler with a circulating system (Neslab CC-100 II immersion cooler and 2095 bath circulator) was used to circulate coolant to the pump, cooling coil, and magnetic stirrer. The temperature in the reactor was controlled by flow of water through the heating jacket and cooling coil inside the reactor. The temperature was measured with a thermocouple (Doric Trendicator 400A) and controlled with a temperature controller (Fuji model PYZ4-TCY1-4V). The thermocouple was calibrated using a standard platinum resistance thermometer (Hart Scientific SPRT model 2560). A pressure gauge (Heise CMM 51848) was used to measure the system pressure. The pressure gauge was calibrated with a dead weight tester (Budenburg model 380H).

Polymerization Experiments. The polymerization of 3-undecylbithiophene was carried out in the reactor at 10.5 MPa and 313 K according to the reaction



The conventional solvent for this polymerization is nitrobenzene, with ferric chloride acting as an oxidant, initiator, and dopant.[10] In the present work, ferric triflate was used as the oxidant because it is soluble in supercritical carbon dioxide.[13,14]

A 4:1 mole ratio of oxidant to monomer was used as suggested for the conventional polymerization in nitrobenzene with ferric chloride as the oxidant.[10] The monomer and ferric triflate were placed in separate glass vials in the reactor so as to preclude mixing before introduction of carbon dioxide, and the vessel was then pressurized with carbon dioxide until the desired pressure of 10.5 MPa was attained. The polymerization reaction was allowed to proceed for 1 h, after which the reactor was depressurized and the polymer removed from the vessel. The polymer was then subjected to successive solvent extractions with acetone, methanol, hexane, tetrahydrofuran (THF), and toluene. The major (THF) fraction was used for characterization.

Composite Preparation. A simple two-step batch process was used for the in situ polymerization of 3-undecylbithiophene in porous, cross-linked polystyrene (PS). In the first step, the host polymer was impregnated with ferric triflate as follows: the host polymer and ferric triflate were placed in the reactor in separate vials, and the reactor was pressurized with carbon dioxide until the desired pressure was attained at a set temperature. These conditions were maintained for a length of time necessary for maximum uptake of carbon dioxide (determined in separate experiments according to procedures described elsewhere[12]). In the second step, the oxidant-impregnated host polymer was placed in contact with a mixture of carbon dioxide and monomer (3UBT) until a maximum was reached in the uptake of carbon dioxide into the host polymer matrix. The polymerization of 3-undecylbithiophene occurred in situ inside the polymer host substrate. The vessel was then quickly depressurized and the host substrate weighed to obtain the mass gain due to the poly(3-undecylbithiophene) formed. Elemental analysis was subsequently performed to determine the actual amount of poly(3-undecylbithiophene) present. Finally, the electrical conductivity of the composite sample was measured with a four-point probe. All samples were characterized using an optical microscope, by elemental analysis, and by their UV−vis and ^{1}H NMR spectra.

Results and Discussion

Polymerization. The properties of poly(3-undecylbithiophene) (P3UBT) synthesized in supercritical carbon dioxide were compared with those of the polymer synthesized by the conventional route using nitrobenzene as the solvent and ferric chloride as the oxidant. Molecular weights of the samples were obtained by gel permeation chromatography using THF and a Waters 410 GPC instrument. The weight-average molecular weight (M_w) of the poly(3-undecylbithiophene) synthesized in nitrobenzene was 26 000 g/mol,[10] whereas that of the polymer synthesized in supercritical carbon dioxide was 20 000 g/mol. Although the molecular weight values are similar in the two solvents, the polydispersity index of the polymer synthesized in nitrobenzene was 2.6 whereas that of the sample

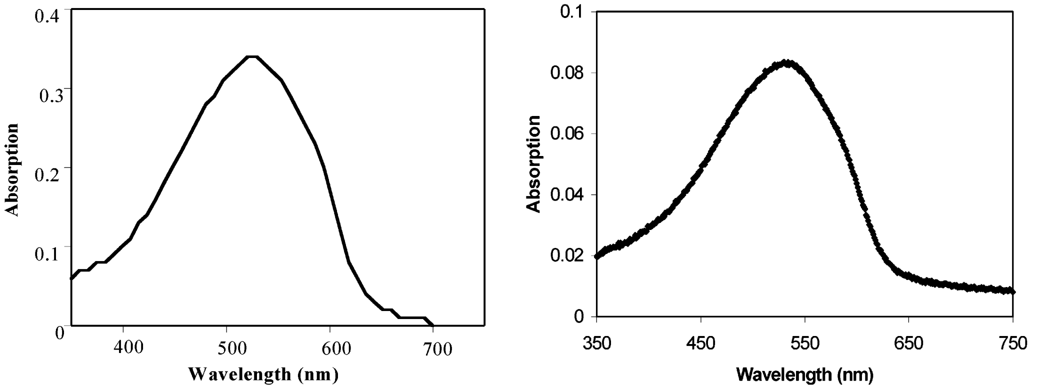


Figure 2. UV−vis spectra of poly(3-undecylbithiophene) synthesized in nitrobenzene[9] (left) and supercritical CO_2 (right).

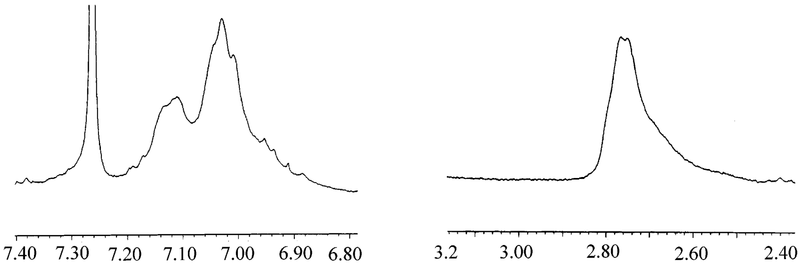


Figure 3. ^{1}H NMR spectra (aromatic and α-CH_2 region) of poly(3-undecylbithiophene) prepared in supercritical CO_2. Spectrum taken in $CDCl_3$, δ [ppm] relative to TMS, signal at $\delta = 7.26$ ppm due to $CHCl_3$.

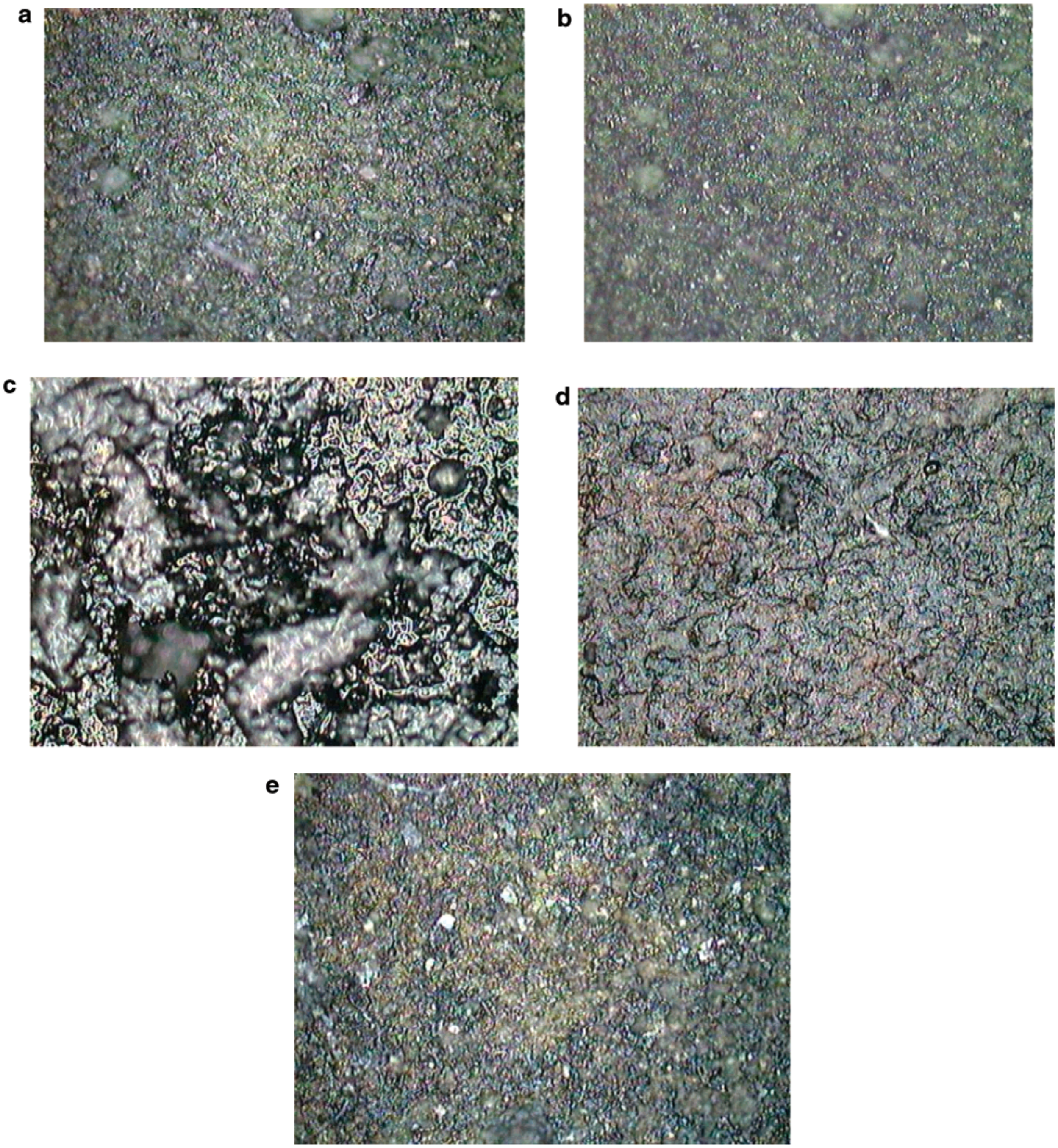


Figure 4. Optical micrographs of composites of P3UBT/PS prepared at (a) 313 K and 10.5 MPa; (b) 363 K and 10.5 MPa; (c) 413 K and 10.5 MPa; (d) 313 K and 20.7 MPa; (e) 313 K and 34.5 MPa. (Each micrograph represents a film that is 1 mm wide at 100× magnification.)

synthesized in supercritical carbon dioxide was 4.7 at the conditions studied. This could be due to the different solubilities of the monomer in the two solvents, the oxidants used, or the conditions of the experiments. The yield of the polymer was approximately 95% after 1 h in supercritical carbon dioxide.

Table 1. Electrical Conductivity, Oxidant (FT) Content, and Conducting Polymer (P3UBT) Content of P3UBT/PS Composites Prepared in Supercritical CO_2

temp (K)	press. (MPa)	FT content (wt %)	P3UBT content (wt %)	av conductivity (S/cm)	std dev (S/cm)
313	10.5	0.2	37.0	2.3×10^{-7}	3×10^{-8}
363	10.5	15.6	30.9	2.2×10^{-6}	5×10^{-7}
413	10.5	5.3	53.9	0	0
313	20.7	8.2	39.0	3.1×10^{-4}	9×10^{-5}
313	34.5	3.7	15.6	2.2×10^{-6}	4×10^{-7}

UV−vis studies were carried out on a film of poly(3-undecylbithiophene) to determine the extent of effective conjugation of the conducting polymer using a Perkin-Elmer Lambda 19 spectrophotometer. The results are shown in Figure 2. The peak in the absorption spectrum (λ_{max}) found at 530 nm compares well with a λ_{max} of 527 nm for the polymer synthesized in nitrobenzene.[10] The extents of effective conjugation are therefore similar in the two cases.

^{1}H NMR spectra were obtained using a Varian XL-400 spectrometer in a $CDCl_3$ solution, and the results are shown in Figure 3. Poly(3-undecylbithiophene) synthesized in supercritical carbon dioxide has a structure very similar to that synthesized in nitrobenzene. The peak in the spectrum at 7.26 ppm is due to the solvent, chloroform, whereas the peaks located between 6.95 and 7.15 ppm are from the protons on the aromatic rings. Finally, the peak located at 2.76 ppm relates to the benzylic methylene protons on the alkyl chain. Essentially the same spectra were obtained by Kowalik et al.[10] for poly(3-undecylbithiophene) synthesized via the conventional route.

The intrinsic electrical conductivity of the poly(3-undecylbithiophene) synthesized in nitrobenzene[10] as well as in carbon dioxide was found to be about 10^{-8} S/cm or in the lower end of the semiconducting range.

Composites Preparation. Composites of poly(3-undecylbithiophene) and porous, cross-linked polystyrene were prepared using supercritical carbon dioxide at 313 K and pressures of 10.5, 20.7, and 34.5 MPa. Experiments were also performed at a constant pressure of 10.5 MPa and temperatures of 313, 363, and 413 K. The results are shown in Table 1 and Figure 4. Although all conductivities were found to be in the semiconducting range, the morphology and electrical conductivity of the composites were greatly influenced by experimental conditions. The highest electrical conductivity was found in the composite prepared at 313 K and 20.7 MPa and the lowest (zero conductivity) in the composite prepared at 413 K and 10.5 MPa. Increasing temperatures correspond to more uptake of oxidant and/or monomer (because of diffusion) and therefore to higher conductivity (Table 1). At significantly higher temperatures, however, twisting of the polymer chains could result in lower conjugation and therefore lower conductivity. This is apparently the case for composites prepared at 413 K. On the other hand, increasing pressures allow more oxidant and/or monomer to be incorporated into the host polymer (because of the higher solvent power of the supercritical solvent), leading to the formation of increasing amounts of conducting polymer and, therefore, to higher conductivity. At the highest pressures studied (34.5 MPa), pneumatic stresses[15] on the polymer could lead to diminished uptake of the oxidant and/or monomer and therefore to lower conductivity.

These arguments are supported by the observed morphology of the composites prepared at various conditions of temperature and pressure in this study. Figure 4 shows optical micrographs of the composite samples. All samples appear to contain significant amounts of the conducting polymer, as evidenced from their dark colors and confirmed by elemental analysis (Table 1). The conducting polymer appears to have been fairly evenly distributed at all conditions (as evidenced from the standard deviations reported in Table 1) except at 413 K. The sample prepared at 413 K shows segregated domains of conducting polymer (Figure 4c) and no conductivity (Table 1). As discussed by Park and Ruckenstein,[6] interconnected networks of conducting polymer are necessary for the composite to exhibit significant electrical conductivity. The highest temperature studied (413 K) does not, therefore, provide an environment for the formation of these interconnected networks. By contrast, the sample prepared at 313 K and 20.7 MPa clearly shows interconnected conducting polymer networks (Figure 4d).

The loading of the conducting polymer in the host polymer must also be sufficient to yield these interconnected polymer networks. Optical micrographs of two samples with different loadings are shown in Figure 5. The sample shown in Figure 5a incorporates 37 wt % poly(3-undecylbithophene) and exhibits an electrical

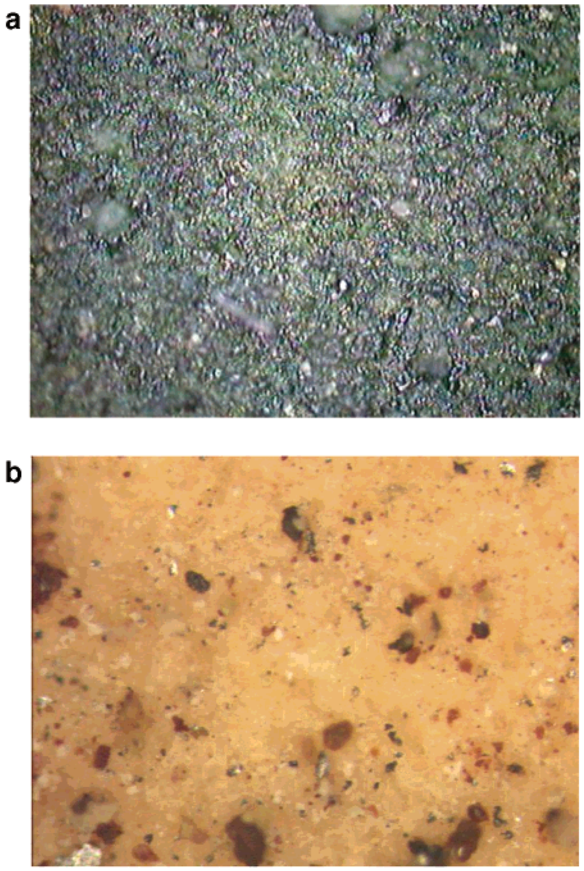


Figure 5. Optical micrographs of P3UBT/PS composites prepared at different loadings of conducting polymer: (a) 37 wt % and (b) 2 wt %. (Each micrograph represents a film that is 1 mm wide at 100× magnification.)

Table 2. Electrical Conductivity of P3UBT/PS Composites at Different Loadings of the Conducting Polymer

reactor conditions	P3UBT content (wt %)	conductivity (S/cm)
low mixing	2	0
high mixing	37	3.1×10^{-6}

conductivity of 3 × 10^{-6} S/cm (Table 2). The sample shown in Figure 5b, on the other hand, incorporates only 2 wt % poly(3-undecylbithiophene) and exhibits no electrical conductivity. Note that both samples were prepared at 313 K and 10.5 MPa, one at high mixing conditions (with stirring) and the other at low mixing conditions (no stirring). Clearly, the amount of conducting polymer incorporated in the host polymer must exceed some threshold value in order to obtain connectivity of the conducting domains necessary for electrical conductivity.

Conclusions

Our studies show that supercritical carbon dioxide is a promising solvent for polymerization of poly(3-undecylbithiophene) as well as the preparation of electrically conducting composites of poly(3-undecylbithiophene) and porous, cross-linked polystyrene. Poly(3-undecylbithiophene) synthesized in supercritical carbon dioxide (with ferric triflate as the oxidant) is similar to the polymer synthesized in nitrobenzene (with ferric chloride as the oxidant) in terms of structure, molecular weight, conjugation, and intrinsic electrical conductivity. Supercritical carbon dioxide also provides a convenient medium for the preparation of composites of poly(3-undecylbithiophene) and porous, cross-linked polystyrene. The experimental conditions (pressure and temperature) can be tuned to optimize the morphology and electrical conductivity of the composite. In the present work, the highest conductivity of 3 × 10^{-4} S/cm was obtained in composites prepared at 313 K and 20.7 MPa, which represent conditions that lead to significant deposition of the oxidant and formation of interconnected conducting polymer networks. Also, the loading of the monomer/conducting polymer must exceed some threshold value in order to provide connectivity of the conducting polymer domains in the host polymer.

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